



# Functionalizing Cu nanoparticles with fluoric polymer to enhance $C_{2+}$ product selectivity in membraned $CO_2$ reduction

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## ABSTRACT

Copper-based nanomaterials are attractive in  $CO_2$  electroreduction into valuable chemicals but still suffer from limited selectivity of  $C_{2+}$  products due to the parasitic hydrogen evolution reaction and inefficient dimerization of adsorbed CO intermediate (\*CO). Herein, we report an in situ polymerization strategy to coat hydrophobic polymer containing methoxyl silane ( $(CH_3O)_3Si-$ ) and trifluoromethyl ( $-CF_3$ ) functional groups on Cu nanoparticles. The optimized Cu-poly exhibits a high Faradaic efficiency of 71.08 % and a remarkable partial current density of  $355.4 \text{ mA cm}^{-2}$  for  $C_{2+}$  products in a membrane electrode assembly electrolyzer using a bicarbonate electrolyte. A combined study of density functional theory calculations and in situ infrared characterizations indicates that the enhanced performances could be ascribed to the decreased formation energy of \*COCO<sub>H</sub>, induced by the withdraw-electron effect of  $-CF_3$  and enhanced coverage of \*CO. This work offers a new insight in tuning the electrocatalytic microenvironment through the surface polymerization process.

## 1. Introduction

Electrochemical  $CO_2$  reduction reaction ( $CO_2RR$ ) to value-added fuels and chemicals from clean electricity generated by renewable sources such as wind and solar is an attractive way of energy storage and conversion [1,2]. Among various metals (e.g., Ag, Au, Sn, Cu, etc.) explored so far, Cu is the only metal that can balance the adsorption of \*CO and \*H intermediates due to its unique electronic properties, thus strongly reducing  $CO_2$  into  $C_{2+}$  products including ethylene ( $C_2H_4$ ), ethanol (EtOH), and propanol (PrOH) [3–6]. However, the competitive hydrogen evolution reaction (HER) and weak \*CO dimerization in aqueous electrolytes still limit the dimerization process and thus the formation of  $C_{2+}$  products [7]. To date, tremendous efforts have been devoted to tailoring the catalytic activity of Cu-based catalysts in  $CO_2RR$ , such as morphology [8,9], facets [10–12], oxidation state [13, 14], particle size [15,16], and so on. Among them, modification of the catalytic microenvironment is of particular interest in tuning local pH and the concentration of intermediates, which can promote

electrode/electrolyte performances for enhanced  $C_{2+}$  selectivity [17–21].

In addition to the selectivity, the partial current density of  $C_{2+}$  products on Cu is also an important factor for practical  $CO_2RR$  applications. The low solubility of  $CO_2$  in water (35 mM at 298 K and 1 atm pressure) and the thick diffusion layer of  $CO_2$  mass transfer make it difficult in H-type cell to meet industrial current requirements [22,23]. Previous studies have shown that zero-gap membrane assembly electrodes (MEA) can achieve ampere-scale current densities, benefiting from the reduced mass transfer resistance and diffusion pathway of gaseous  $CO_2$  [24,25]. Although the catholyte-free design greatly alleviates the formation of carbonate precipitates in neutral or alkaline electrolytes as compared to flow cell, parasitic HER and unexpected salt precipitates exist in MEA configurations due to two factors. Firstly, the  $CO_2RR$  is a proton-consumption reaction that can create a strongly alkaline microenvironment, which induces to form hydroxide deposits. Secondly, cations from anolyte can pass through the anion-exchange membrane to react with local hydroxyls under the driving force of an

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applied electric field [26]. Moreover, the formation of salt precipitates can reduce the CO<sub>2</sub> utilization and overall energy efficiency of MEA devices. Thus, the management of water and salt in MEA electrolyzer is desirable. Of particular note, tuning interfacial water on the surface of gas diffusion layer (GDL) is the focus to solving the problem of competitive HER and salt formation. Furthermore, water can also affect the distribution of products on the gas diffusion electrode (GDE) [27, 28]. Introducing hydrophobic nanoparticles into the catalysts layer and coating the catalyst surface with hydrophobic organic molecules have proven effective to improve the hydrophobicity of GDL [29–33]. In spite of substantial progress, it remains challenging to simultaneously control the hydrophobicity and surface oxidation state of Cu-based catalysts.

In this work, we report a hydrophobic modification catalyst consisting of Cu nanoparticles and fluorine polymers (Cu-poly), which serves as an efficient catalyst for catalyzing CO<sub>2</sub> into C<sub>2+</sub> products. A combined experimental/computational study demonstrates that the fluorine polymers functionalized Cu-poly enhances the coverage of \*CO species and decreases the formation energy of the key intermediates (\*COCO) by the hydrogen bond. As a result, the prepared Cu-poly catalysts shows an improved Faradaic efficiency (FE) of 71.08 % for C<sub>2+</sub> hydrocarbons at −3.98 V, as compared to bare Cu (FE<sub>C<sub>2+</sub></sub> 61.59 %). This work proposes a facile surface polymerization pathway to tune the electrocatalytic microenvironment in the reduction of CO<sub>2</sub> to C<sub>2+</sub> products and would provide new insight into addressing the selectivity challenges in practical CO<sub>2</sub>RR at industrial scale.

## 2. Experimental section

### 2.1. Chemical reagents

All chemicals and reagents were purchased from commercial sources and used without further treatment. Cu nanoparticles (Cu 99.5 %) were purchased from Sigma-Aldrich (Shanghai) Trading. N-N-dimethylacetamide (DMAC, AR, 99.0 %) and absolute ethanol (99.5 %) were purchased from the Shanghai Aladdin Biochemical Technology. 2,2,2-trifluoroethyl methacrylate (TFEMA, 98.0 %) and 3-methacryloxypropyltrimethoxysilane (MAPTMS, 97.0 %) were purchased from Anhui Senrise Technology. 2,2-azobis (2-methylpropionitrile) (AIBN, 98.0 %) and deuterium oxide (D<sub>2</sub>O, 99.9 %) were purchased from Adamas-Beta (Shanghai) Chemical Reagent. Dimethyl sulfoxide (DMSO, 99.0 %) and potassium bicarbonate (KHCO<sub>3</sub>, ≥99.99 %) were obtained from Shanghai Macklin Biochemical. Ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9 H<sub>2</sub>O, 98.0 %) was purchased from the Xiya Chemical Technology (Shandong). Nafion D-521 dispersion (5 % W/W in water and 1-propanol, exchange capacity ≥ 0.92 meq/g) was bought from Alfa Aesar China Chemical. Ni foam was purchased from Tianjin Eilian Electronics & Technology. Anion-exchange membrane (AEM, X37-Grade 50 RT) and the GDL (YLS-30 T), which consists of a carbon fiber paper and a microporous layer surface coating with poly (tetrafluoroethylene) (PTFE) hydrophobic treatment, were purchased from Dioxide Materials. All the electrolytes were prepared using ultrapure water (18.2 MΩ cm<sup>−1</sup>).

### 2.2. Synthesis of polymer modified Cu NPs

Cu-poly-1 was prepared by following previous report with a slight modification [34]. Briefly, 100.0 mg Cu NPs were ultrasonically dispersed in 20.0 mL of DMAC for 5 min. Then 87.0 μL MAPTMS and 750.0 μL TFEMA were rapidly added to the above dark solution and ultrasonication for another 30 min. After that, 6.0 mg AIBN was added to the above suspension, and the reactor was placed in an oven at 75 °C for 4 h. The dark catalyst was then collected by centrifugation and washed three times with ethanol and dried in a vacuum oven at 80 °C overnight. Cu-poly-2 was prepared with similar procedures, except that the additive amounts of MAPTMS and AIBN were increased to 325.0 μL and 20.0 mg, respectively.

### 2.3. Characterizations

The crystal phase was identified by powder X-ray diffraction (XRD, MimFlex600, Rigaku, Japan) spectroscopy with Cu Kα radiation (40 kV, λ = 1.5406 Å and 15 mA) at a scan rate of 10 min<sup>−1</sup> with the 2-Theta degree from 5° to 85°. The composition, microstructure and morphology were investigated on Raman spectroscopy (InVia Reflex, Renishaw, UK), Fourier transform infrared (FTIR) reflection spectroscopy (Nicolet iS50, Thermo Fisher Scientific, USA), field emission scanning electron microscopy (SEM, JSM-7900F, JEOL, Japan) at an accelerating voltage of 1.0 kV, and high-resolution transmission electron microscopy (HRTEM, Talos F200X G2, FEI Czech Republic) equipped with energy dispersive X-ray spectroscopy (EDS). Nitrogen and carbon dioxide adsorption/desorption measurements were conducted on a Micromeritics ASAP 2460 Analyzer (USA). Pore volumes and pore sizes were calculated by the pore-size distribution curves from the desorption isotherms using the density functional theory (DFT) methods. The valence states of samples were analyzed using X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd, UK). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images were collected on JEOL JEM-ARM200F NEOARM equipped with aberration corrector for STEM. The microscope was operated at 200 kV. Elemental analysis was performed on elemental analyzer (vario EL CUBE, elemental, Germany).

### 2.4. Preparation of cathode and anode

GDL: GDL serves as a cathodic catalyst support and consists of hydrophobic macroporous carbon nanofibers (Fig. S1a) with hydrophobicity and high gas permeability, and conducting carbon black (Fig. S1b).

Cathode preparation: For CO<sub>2</sub>RR cathode preparation, 60.0 mg catalysts and 60.0 μL Nafion solution were mixed in 3.0 mL ethanol and sonicated for 1 h to prepare catalyst ink. The prepared ink was sprayed on 2.89 cm<sup>2</sup> of hydrophobic GDL and the loading of the catalyst was adjusted to ~1.0 mg cm<sup>−2</sup>.

Anode preparation: According to previous report, nickel iron layered double hydroxide (NiFe LDH) was synthesized by wet chemical etching with a slight modification [35]. Typically, a piece of Ni foam (1.9 × 1.9 cm) was pre-cleaned with 5 wt% HCl for 1 h under ultrasonication and then washed by deionized water and ethanol. After that, 60.0 mg Fe(NO<sub>3</sub>)<sub>3</sub>•9 H<sub>2</sub>O was dissolved in 20.0 mL H<sub>2</sub>O and sonicated for another 30 min. Then, Ni foam was immersed in the above dark red solution and left overnight at room temperature. After treatment, the as-obtained foam was rinsed with water and ethanol for several times to remove residual salts. The treated Ni foam was then dried in an oven at 80 °C overnight for further use.

Pretreatment of AEM: X37-Grade 50 RT membranes were activated in 1 M KOH for 12 h at room temperature and washed three times with ultrapure water before use.

### 2.5. Electrochemical measurements and products qualification

MEA measurements: CO<sub>2</sub>RR measurements were carried out in an MEA electrolyzer (purchased from Suzhou Sinero Technology) equipped with domestic titanium plate electroplated with Au film, which is used as the current collector. The cell consists of anode (NiFe LDH), silicone gasket, AEM and catalysts cathode, and is bolted to prevent gas or liquid leakage or crossover. The pressure of the cell was first stabilized before each electrochemical test. Typically, CO<sub>2</sub> was humidified by bubbling through a glass bottle contained 30.0 mL of water at room temperature and flowed to the cathode of the cell with a gas flow rate of 60.0 mL min<sup>−1</sup>. For the anode, 40.0 mL anolyte of 1 M KHCO<sub>3</sub> was cycled by a peristaltic pump with a flow rate of 6.0 mL min<sup>−1</sup>. A sealed glass vital with 20.0 mL of water in cold trap was used to collect liquid products

such as ethanol, propanol, formate, and acetate [36]. All CO<sub>2</sub>RR electrochemical data were collected using a P4000 electrochemical workstation (Solartron, PAR-Ametek). Gas products were simultaneously analyzed every 11 min using an online gas chromatograph (GC, Shimadzu 2014 C). The GC was equipped with a flame ionization detector (FID) for quantification of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and CO and a thermal conductivity detector (TCD) for H<sub>2</sub>, using Ar as the carrier gas. Liquid products were quantified by <sup>1</sup>H NMR spectroscopy on a 400 MHz spectrometer (Quantum-1, Zhongke-Niujin MR Tech). To record NMR data, 20.0 mL of catholyte from the cold trap was collected and 40.0 mL of anolyte was mixed for further use. A 30.0 mL of electrolyte was taken out from the mixture and then 20.0 μL DMSO was added as an internal standard. Finally, 450.0 μL of the above solution and 50.0 μL D<sub>2</sub>O were transferred to a sample tube and analyzed on NMR spectrometer. The water peak in each spectrum was suppressed using previous method [37]. Faradaic efficiencies were calculated according to the equation [4]:

$$FE_x(\%) = \frac{n_x \times n_{ex}^- \times F}{Q} \times 100$$

where  $n_x$  is the amount (mol) of product  $x$ ,  $n_{ex}^-$  is the number of electron to form  $x$  from CO<sub>2</sub>/H<sub>2</sub>O,  $F$  is the Faraday constant (94685 C mol<sup>-1</sup>), and  $Q$  is the charge passed to generate  $x$ .

The products formation rate ( $r$ , μmol cm<sup>-2</sup> h<sup>-1</sup>), which represents the quantity of all products obtained per unit of area and time [38], is calculated by the following equation [39]:

$$\text{Formation rate} = (Q_{\text{tot}} \times FE_x) / (96,485 \times n_x \times t \times S)$$

where  $Q_{\text{tot}}$  is the total charge,  $t$  is the electrolysis time (h),  $S$  is the geometric area of the cathode (cm<sup>2</sup>), and  $n_x$  is the molar amount of the products.

## 2.6. In situ infrared spectroscopy

Attenuated total reflection surface-enhanced infrared spectroscopy (ATR-SEIRAS) was conducted using a FTIR spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA) equipped with a Mercury Cadmium Telluride (MCT) detector, which was cooled with liquid nitrogen. The ATR-SEIRAS spectra were recorded at a resolution of 4.0 cm<sup>-1</sup> and a range of 400–4000 cm<sup>-1</sup>, with 32 interferograms collected for each spectrum. Electrochemical measurements were performed using a three-electrode measurement system with Pt foil as the counter electrode and Ag/AgCl as the reference electrode. Fig. S2 illustrates the configuration and digital photograph of in situ ATR-SEIRAS cell. Firstly, Au films were prepared by sputtering Au NPs onto the surface of the Si prism, which plays a key role in enhancing the signal of intermediate species [40]. Then, the catalyst ink containing Cu NPs or Cu-poly catalyst was dropped on the surface of the Au film to form the working electrode. Real-time FTIR spectra were recorded during the chronopotentiometry tests with operating potentials from the open circuit potential to −1.4 V (vs. RHE) in CO<sub>2</sub>-saturated 1 M KHCO<sub>3</sub> solution. The increment of applied potentials was 100.0 mV and the test time was 80.0 s

## 2.7. Calculation methods and models

DFT calculations were performed by Vienna ab initio simulation package (VASP) using the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange–correlation functional (GGA-PBE) for describing the interactions in the absence of magnetic moments [41, 42]. Van der Waals interactions were included using the DFT+D3 approach developed by Grimme, with zero damping. The electronic iterations convergence was set to 1 × 10<sup>-6</sup> eV using the Fast (Davidson and RMM-DIIS) algorithm and reciprocal space projection operators. The plane-wave cutoff energy was set to 400.0 eV with a 1 × 1 × 1 mesh and k-spacing of 0.5 per Angstrom. The k-mesh was centered on the gamma point. First-order Methfessel–Paxton smearing with a width of

0.2 eV was employed in the calculations. The accuracy of calculations was verified by ensuring that the convergence criteria were met. We used a 6 × 6 four-layer periodic model of Cu (111) to simulate the surface, and 15 Å was selected as the vacuum layer [43]. In the model, surface relaxation was considered. Only the top two layers were permitted to relax during the optimization stage. While the bottom two levels were fixed, the top two layers were movable. A trimer is composed of three types of monomers, which is used to simplify the simulation of high molecular copolymer and is placed on the surface of Cu for adsorption calculation.

## 3. Results and discussion

### 3.1. Catalysts preparation and characterizations

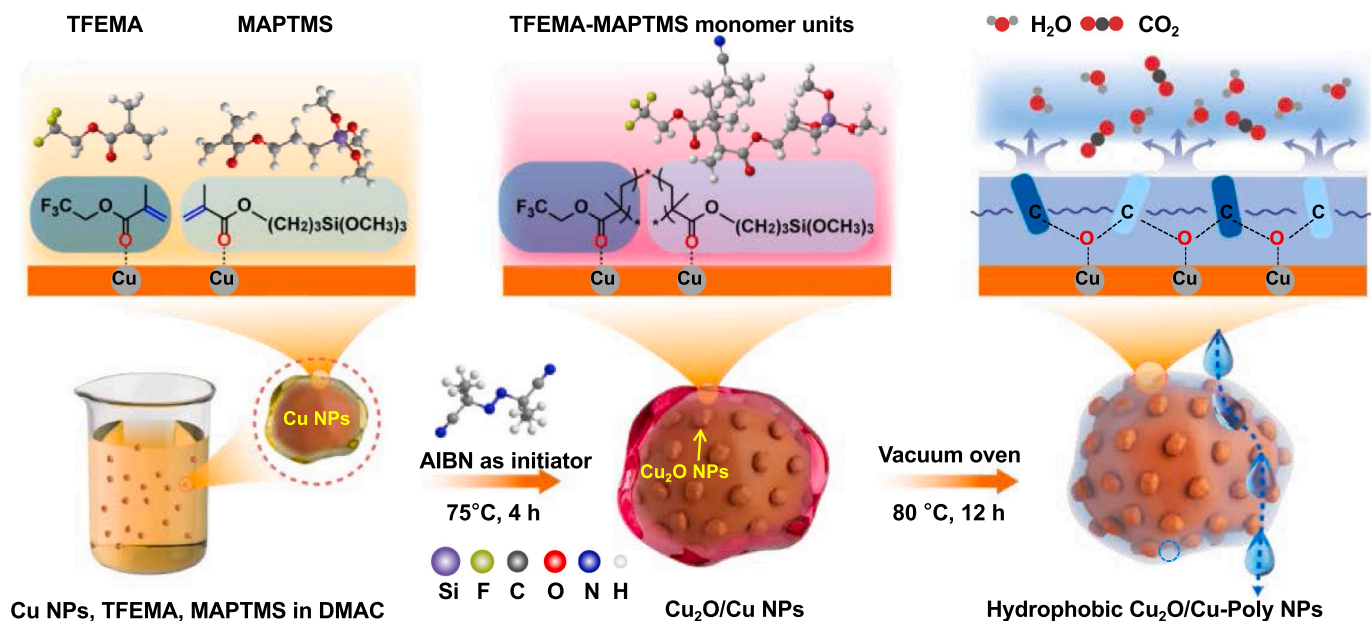
The Cu-poly was prepared by an in situ polymerization process [34]. Scheme 1 shows the procedures of the synthesis of Cu-poly catalysts. Briefly, Cu NPs, TFEMA with −CF<sub>3</sub> groups and MAPTMS with (CH<sub>3</sub>O)<sub>3</sub>Si− groups were mixed uniformly in DMAC by ultrasonication and then polymerized under the initiation of injecting AIBN. The polymer in Cu-poly-1 is composed of 1-(2,2,2-trifluoroethyl) 5-(3-(trimethoxysilyl)propyl) 2-(2-cyano-2-methylpropyl)–2,4-dimethylpentane dioate (abbreviated as TFEMA-MAPTMS, Fig. S3) monomers and is connected with Cu by covalent coordination effect originated from the unshared pair electrons of oxygen in carbonyl functional groups (Fig. S4). As shown in SEM and TEM images (Fig. S5), the bare Cu NPs possess an irregular morphology with aggregation of particles. While the morphology is largely maintained, the size of primary particles in Cu-poly-1 is much smaller than that of the pristine Cu NPs possibly due to the partial etching of Cu during polymerization process (Fig. 1a and Fig. S6). Besides, the polymer layer featuring a different monomer structure (Fig. S7) in Cu-poly-2 is much thicker with apparently higher ratio of carbon than that of Cu-poly-1 (Fig. S8 and Table S1), which indicates that the thickness and composition of the polymer could be regulated by adjusting the amount of reactants.

The Cu-poly-1 catalyst presents a polymer layer-wrapped polycrystalline structure containing Cu and Cu<sub>2</sub>O, as evidenced by the HAADF-STEM images (Fig. 1b) and the concentric rings and bright discrete diffraction spots in the corresponding selected-area electron diffraction (SAED) patterns (Fig. 1c). Lattice fringes of an enlarged nanoparticle feature an interplanar distance of 0.24 nm (Fig. 1b inset), which is attributed to the (111) crystal plane of Cu<sub>2</sub>O [44,45]. The coated polymer layer can be seen on different crystalline NPs in Cu-poly-1 (Fig. S9). Additionally, EDS mapping reveals uniform distribution of Cu, Si, F, C, and O after polymerization on Cu catalysts (Fig. 1d and Fig. S10). Furthermore, contact angle (CA) measurements indicate that the as-prepared Cu-poly-1/2 possess a significantly more hydrophobic surface than bare Cu due to the organic functional groups of the polymer (Fig. S11). The hydrophobicity of catalysts would suppress hydrogen evolution reaction (HER) while benefit to reduce the thickness of CO<sub>2</sub> gas diffusion layer and promote the mass transfer kinetics of CO<sub>2</sub> [46,47].

### 3.2. Phase structure and surface oxidation

The crystal phase structures of different catalysts were characterized by powder XRD. The bare Cu NPs and Cu-poly-1/2 samples show similar diffraction patterns, which can be readily assigned to a major phase of Cu and a minor phase of Cu<sub>2</sub>O (Fig. 2a). As compared to Cu NPs, the relative intensity of Cu<sub>2</sub>O (111) peak by normalizing to Cu (111) peaks is enhanced in Cu-poly-1/2 (Fig. S12), suggesting a higher ratio of Cu<sub>2</sub>O due to the presence of carbonyl groups in polymerization. The presence of more oxidized Cu would result in a moderate affinity of \*CO species that favors C–C coupling [48,49]. Anchoring polymers on the surface of Cu NPs can be evidenced from the FTIR spectroscopies (Fig. 2b). The strong absorption band at 1748 cm<sup>-1</sup> of Cu-poly-1/2 can be attributed to





**Scheme 1.** Schematic illustration for the preparation of hydrophobic polymer-coated Cu catalysts.

the  $\text{C}=\text{O}$  stretching vibration of the polymer and the vibration at  $628\text{ cm}^{-1}$  corresponds to  $\text{Cu}-\text{O}$  bonds [34]. Also, the signal belong to carbonyl stretching can be identified in the spectra of MAPTMS and TFEMA (Fig. S13a).

For comparison, Cu NPs treated with single monomer (i.e., MAPTMS or TFEMA) were also prepared and characterized. As expected, Cu-MAPTMS and Cu-TFEMA catalysts show analogous FTIR spectra at  $1748\text{ cm}^{-1}$  without  $\text{C}=\text{O}$  groups (Fig. S13b), suggesting that polymerization requires the addition of both MAPTMS and TFEMA molecules. Comparing the infrared data of monomers and Cu-poly-1/2 indicates that the coated polymeric layer is composed of TFEMA-MAPTMS copolymer. Additionally, the main peaks at 274 and  $594\text{ cm}^{-1}$  in the Raman spectra could be attributed to the vibration of the  $\text{Cu}-\text{O}$  bonding (Fig. 2c). Collecting XRD, FTIR and Raman results confirms the increase of oxidized Cu species after polymerization on Cu NPs.

In survey XPS spectra, F is observed in Cu-poly-1/2 rather than bare Cu (Fig. S14), indicating the presence of  $-\text{CF}_3$  functional groups in the polymer. High-resolution spectra of F 1s and Si 2s spectra reveal the formation of fluorine and silicic polymers (Fig. 2d). It is worth noting that the binding energy of Cu  $2p_{3/2}$  in Cu-poly-1/2 ( $930.2\text{ eV}$ ) is higher than that of bare Cu NPs ( $929.6\text{ eV}$ ), as shown in Fig. 2e. Moreover, Cu Auger LMM spectra further show a higher binding energy of Cu in Cu-poly-1/2 than that of Cu NPs (Fig. S15). These results again indicate that more surface Cu was oxidized after the polymeric modification, which is favorable to the C–C coupling.

To characterize the texture of Cu and Cu-poly-1/2 catalysts,  $\text{CO}_2$  and  $\text{N}_2$  adsorption/desorption isotherm curves were recorded in an ice-water mixture and a liquid nitrogen bath, respectively. The higher amount of adsorbed gas in Cu-poly-1/2 than Cu clearly indicates enriched porous structures in the presence of polymers (Fig. 2f and Fig. S16). The determined specific surface area of Cu-poly-1/2 is also higher than that of Cu NPs (Fig. S16), which is due to the increased dispersity of Cu NPs induced by polymerization processing. Enhanced adsorption capacity would enrich the local concentration of  $\text{CO}_2$  on the catalyst surface, contributing to increase of the total  $\text{CO}_2\text{RR}$  current density [29,30].

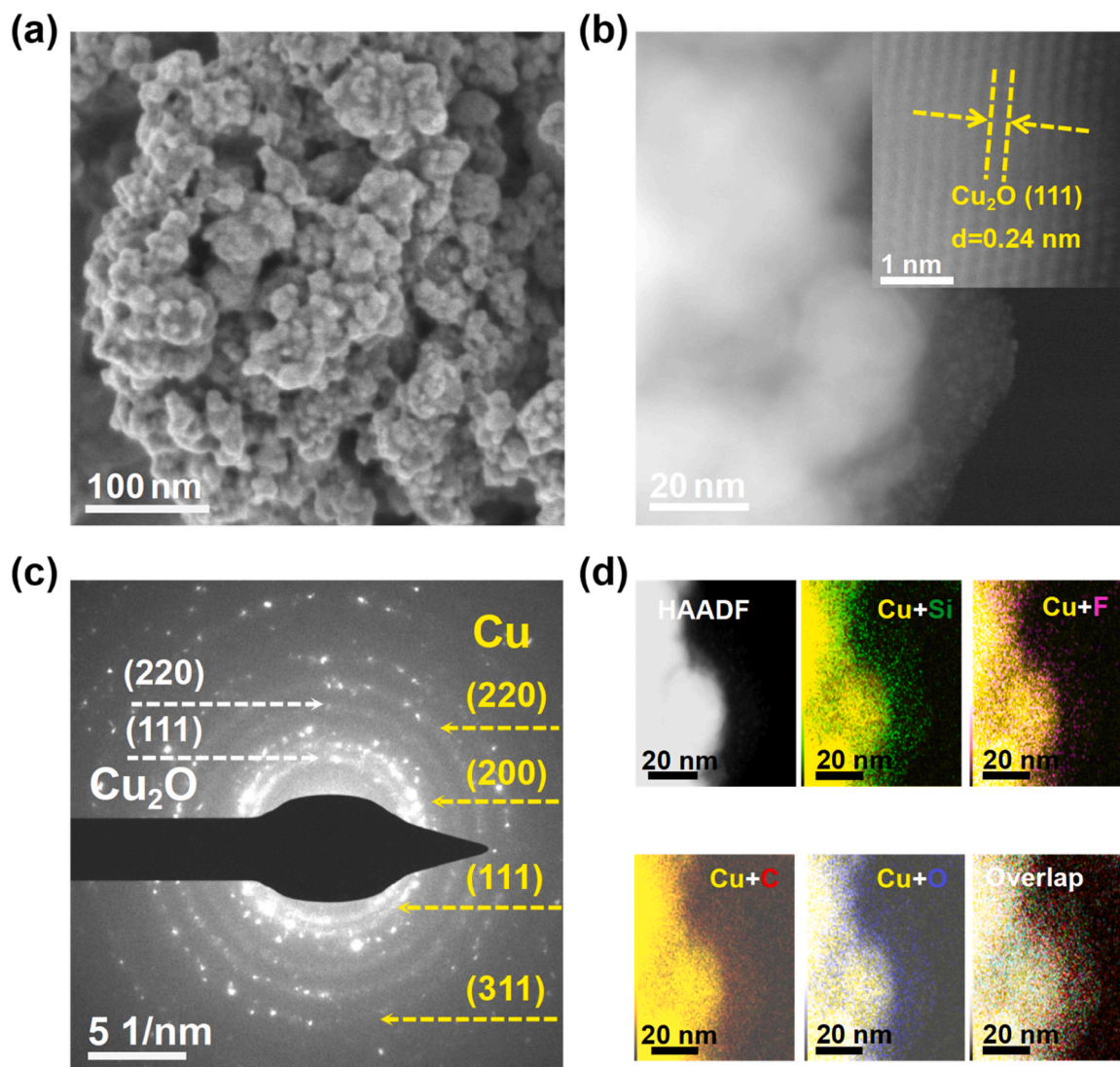
### 3.3. MEA cell measurements for $\text{CO}_2\text{RR}$

The products distribution on Cu, Cu-poly-1/2 were evaluated by adopting a MEA device with characteristics of the zero-gap, catholyte-

free and gas-direct electrolysis [50]. Fig. 3a shows the schematic configuration of assembled MEA cell. Gas diffusion electrode (GDE) is composed of a GDL and a catalysts layer (CL) of Cu or Cu-poly-1/2. As seen from the SEM images, the GDE features a thickness of  $\sim 5.0\text{ }\mu\text{m}$ , a porous structure and a rough surface (Fig. S17), which would favor the accessibility of electrolytes. Additionally, the three-dimensional contour plane profiles show that the catalyst is distributed uniformly in the electrode (Fig. S18). Intentionally, the area of GDE is slightly smaller than that of anode of NiFe LDH ( $2.89$  vs  $3.61\text{ cm}^2$ ), aiming to achieve the maximal cathode utilization (Fig. S19). Flower-like NiFe LDH, with a superior oxygen evolution reaction (OER) activity compared with neat Ni foam in neutral electrolytes, is used as the counter electrode of  $\text{CO}_2\text{RR}$  cell (Fig. S20).

As shown in the linear sweep voltammetry (LSV) curves of Cu and Cu-poly-1/2, there is a slight decrease of total current density on polymer-modified Cu compared with bare Cu at the same potential, which is ascribed to the decreased electrochemically active surface area (Fig. S21 and S22). The composition of gaseous products was analyzed every 11 min by an online GC using chronopotentiometry from 300 to  $550\text{ mA cm}^{-2}$ . For Cu-poly-1, the FE of  $\text{H}_2$  fluctuates from 10.10 % at  $400\text{ mA cm}^{-2}$  to 25.53 % at  $550\text{ mA cm}^{-2}$ . Meanwhile, the FE of  $\text{C}_2\text{H}_4$  increases from 28.59 % at  $300\text{ mA cm}^{-2}$  to 41.80 % at  $450\text{ mA cm}^{-2}$  (Fig. 3b). In comparison, the FE of  $\text{H}_2$  for bare Cu NPs fluctuates from 20.93 % at  $450\text{ mA cm}^{-2}$  to 32.70 % at  $550\text{ mA cm}^{-2}$ , while the FE of  $\text{C}_2\text{H}_4$  varies from 24.62 % at  $300\text{ mA cm}^{-2}$  to 35.15 % at  $500\text{ mA cm}^{-2}$  (Fig. 3c). Similarly, Cu-poly-2 shows the same trend as Cu-poly-1 (Fig. S23). These integral improvements of  $\text{C}_2\text{H}_4$  production are mainly due to the enhanced coverage of  $\text{*CO}$  species, limited diffusion of  $\text{H}_2\text{O}$  and elevated interfacial concentration of  $\text{CO}_2$  [51]. The polymer layer tends to prevent  $\text{H}_2\text{O}$  from flooding the surface of Cu-based catalysts due to the strong hydrophobicity of abundant silanic functional groups [34]. Meanwhile, the aerophilic characteristic would decrease the diffusion resistance of  $\text{CO}_2$  and accelerate the  $\text{CO}_2$  mass transfer dynamics [29]. In addition, the  $\text{CO}_2$  enrichment near the surface of polymer modified Cu-based catalysts would promote the production of more  $\text{*CO}$  species, since the subsequent protonation reaction is limited due to the lack of sufficient proton source ( $\text{H}_2\text{O}$ ) [52].

Besides gaseous products, liquid products generated from Cu NPs and Cu-poly-1/2 were collected at different current densities by employing the self-designed cold trap and analyzed by NMR. We also collected and analyzed the anolyte because of the possible crossover of



**Fig. 1.** (a) The SEM images, (b) the HAADF-STEM image, (c) SAED pattern, and (d) elemental mapping images of Cu-poly-1. Inset of (b) shows the corresponding HRTEM image of a nanoparticle. Color in (d): Cu yellow, Si green, F purple, C red, O blue.

the products driven by the electric field (Fig. S24). For all the three Cu-based electrodes, ethanol and propanol are the main liquid products. However, the FE of ethanol on Cu-poly-1/2 is higher than that on Cu NPs. At current density of  $500 \text{ mA cm}^{-2}$ , the  $\text{FE}_{\text{C}_2+}$  is 71.08 % and 64.22 % for Cu-poly-1 and Cu-poly-2, respectively, exceeding that of bare Cu (61.59 %) (Fig. 3d). It should be noted that the total FE of all gas and liquid products detected in each measurement is less than 100 % due to the loss of accumulated flow amount, which is caused by the frictional resistance of gas products flow across the pipes (Fig. S25) [53]. Furthermore, the difference in activity and selectivity between the two polymer-coated catalysts can be explained by two factors. Firstly, the content of oxidized Cu is lower in Cu-poly-1 than in Cu-poly-2, as revealed by XRD, Raman and CV curves (Fig. 2a,c and Fig. S26). The oxidation state of Cu exerts large effect on the selectivity of products in the  $\text{CO}_2\text{RR}$  on Cu-based electrocatalysts [54,55]. Secondly, the polymer layer in Cu-poly-1 is thinner than that of Cu-poly-2, which affects the local concentration of the reactants ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) and thus the products distribution [56].

To evaluate the performance of polymer-coated catalysts, Table S2 compares the catalytic performances in terms of FE and current density of  $\text{C}_2+$  products for Cu-poly-1 and previous  $\text{CO}_2\text{RR}$  electrocatalysts using

the MEA cell. The products formation rates are also summarized in Table S3. Notably, the maximum value of FE and current density of  $\text{C}_2+$  products for Cu-poly-1 are 71.08 % and  $-355.4 \text{ mA cm}^{-2}$ , respectively, at the applied cell voltage of  $-3.98 \text{ V}$ . Besides, the corresponding maximum formation rate of  $\text{C}_2+$  products is  $1114.99 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ . These values are comparable to previously reported state-of-the-art  $\text{CO}_2\text{RR}$  catalysts. In addition to activity and selectivity, the stability of bare Cu and polymer-modified Cu NPs was investigated by SEM and TEM after  $\text{CO}_2$  electrolysis. The nanoparticle morphology and porous texture are maintained in Cu, Cu-poly-1/2 catalysts (Fig. S27). The coated polymer layer and the oxidized Cu phase were also observed for both Cu-poly-1 and Cu-poly-2 catalysts (Fig. S28-30). Furthermore, the crystal planes of Cu (111) and  $\text{Cu}_2\text{O}$  (111) are visualized in tested bare Cu (Fig. S31). Then, the XPS spectra of Cu NPs and Cu-poly-1/2 catalysts after  $\text{CO}_2\text{RR}$ , operated at different current densities, were recorded to investigate the chemical states of Cu. The results indicate that both metallic Cu and oxidized Cu species exist in all three samples after  $\text{CO}_2\text{RR}$  (Fig. S32).

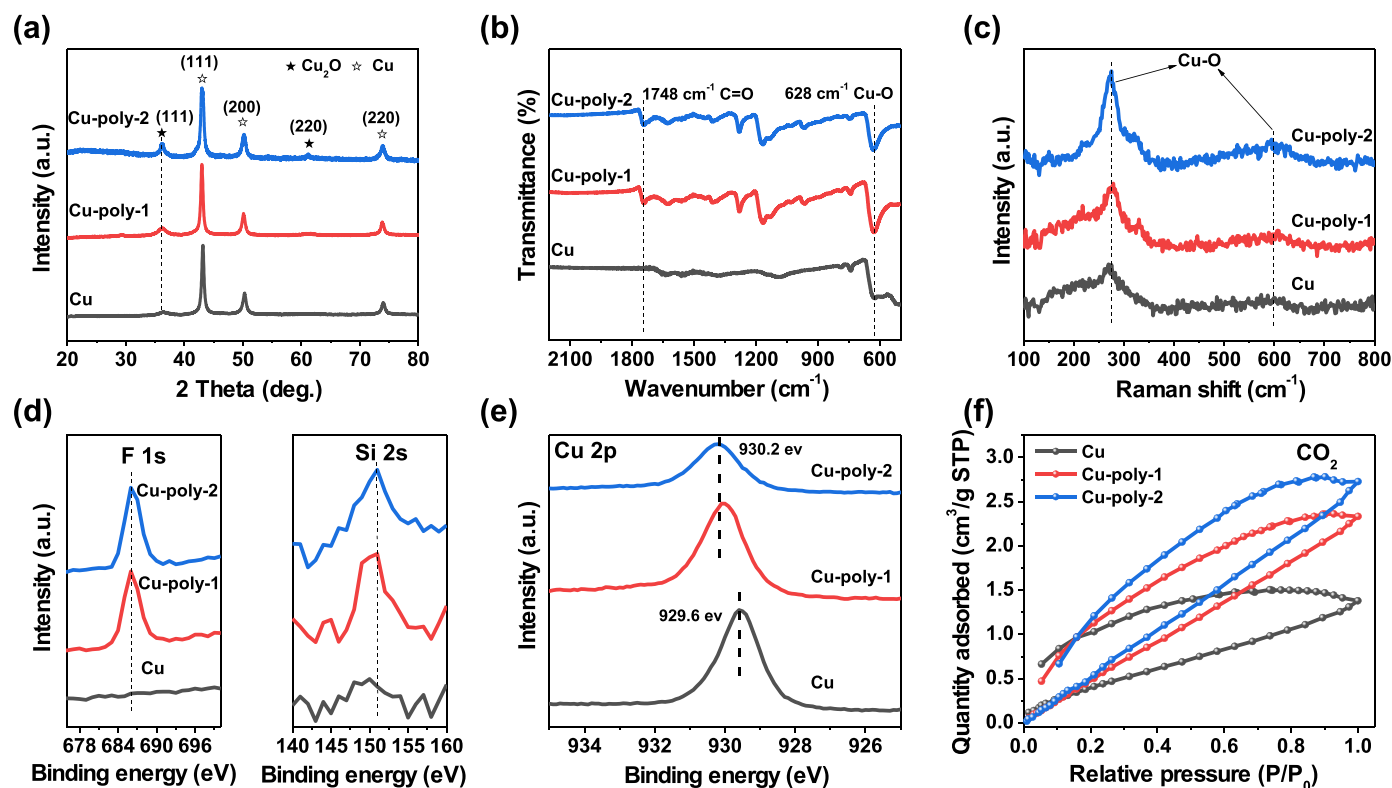


Fig. 2. (a) The XRD patterns, (b) FTIR spectra, (c) Raman spectra, (d) F 1s and Si 2s XPS spectra, (e) Cu 2p spectra, and (f) CO<sub>2</sub> adsorption/desorption curves of Cu NPs, Cu-poly-1, and Cu-poly-2.

### 3.4. In situ FTIR analysis

To gain a deep insight into the reaction mechanism, in situ ATR-SEIRAS spectroscopy was adopted to investigate the evolution of intermediates adsorbing on the surface of the catalysts. Fig. 4a and b show the real-time FTIR spectra of CO<sub>2</sub>RR recorded on Cu and Cu-poly-1, respectively. An apparent band is detected from 2110 to 2080 cm<sup>-1</sup>, which should be assigned to the stretching vibration of the linearly adsorbed \*CO species,  $\nu(\text{CO}_\text{L})$  [57,58]. Meanwhile, the observed Stark effect of  $\nu(\text{CO}_\text{L})$  indicates that the applied potential would affect the vibration of \*CO species during CO<sub>2</sub>RR [59,60]. Particularly, the peak area of adsorbed CO<sub>L</sub> is larger on Cu-poly-1 as compared to Cu NPs (Fig. 4a and b), suggesting increased coverage of \*CO on polymer-modified Cu. As shown in Fig. 4c, Cu-poly-1 shows a lower wavenumber of \*CO than that of Cu. Besides, the narrowing of the bandwidth of  $\nu(\text{CO}_\text{L})$  on Cu-poly-1 is also investigated, which indicates that the CO<sub>L</sub> appeared to adsorb on Cu-poly-1 with a more ordered pattern and thus to provide a high possibility of C–C polymerization (Fig. S33) [51]. This spectroscopic analysis reveals the mechanism of the enhanced multicarbon products selectivity of Cu-poly-1 as compared to bare Cu NPs (Fig. 4d). In conclusion, Cu-poly-1 presents a relative high coverage of \*CO as compared to bare Cu, which is beneficial to the dimerization of \*CO and further to generate C<sub>2+</sub> products [61].

### 3.5. DFT study on reaction mechanism

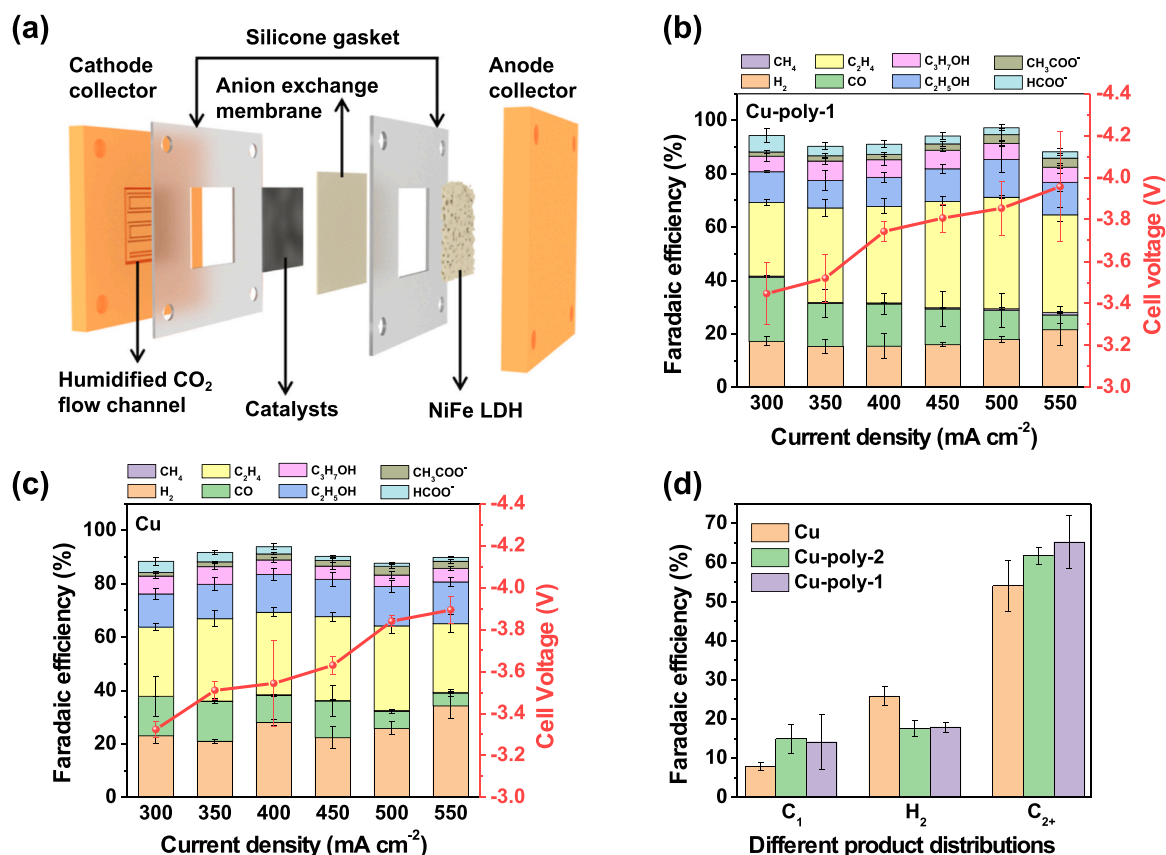
DFT calculations were further conducted to reveal the effect of polymer on the adsorption energy of \*CO and formation energy of \*COCOH intermediates over Cu NPs and polymer modified Cu (Cu-poly). The optimized configurations of adsorbed \*CO show that the bond length of Cu–CO on Cu-poly slightly increases as compared to Cu NPs (1.858 vs 1.848 Å), which is caused by the electrostatic interaction and the weak steric hindrance of the polymers (Fig. 5a, Fig. S34 and S35). In

addition, the adsorption energy of \*CO on Cu NPs is more negative as compared to Cu-poly (–1.44 vs. –1.03 eV, Fig. 5b), indicating that the \*CO species prefer to stably adsorb on Cu sites and are difficult to release, which is more favorable to the subsequent hydrogenation (forming C<sub>1</sub> products) instead of C–C polymerization to generate C<sub>2+</sub> species [54,62]. Furthermore, the optimized models of \*COCOH intermediates adsorbing on Cu NPs and Cu-poly suggest the formation of hydrogen bonds between the –CF<sub>3</sub> functional groups and \*COCOH species (Fig. 5c, Fig. S36 and S37) [63]. Thus, the formation energy of \*COCOH on Cu-poly is lower than that of Cu NPs (2.27 vs. 2.37 eV), which indicates that the polymer modified Cu is favorable to form C<sub>2+</sub> species rather than C<sub>1</sub> hydrocarbons (Fig. 5b). Fig. 5d shows the proposed reaction pathway for CO<sub>2</sub>RR to C<sub>2+</sub> products on Cu-poly catalysts. Consequently, Cu-poly-1 with sufficient \*CO coverage and relatively low \*COCOH formation energy prefers to enhance the C–C coupling and thus the formation of C<sub>2+</sub> products.

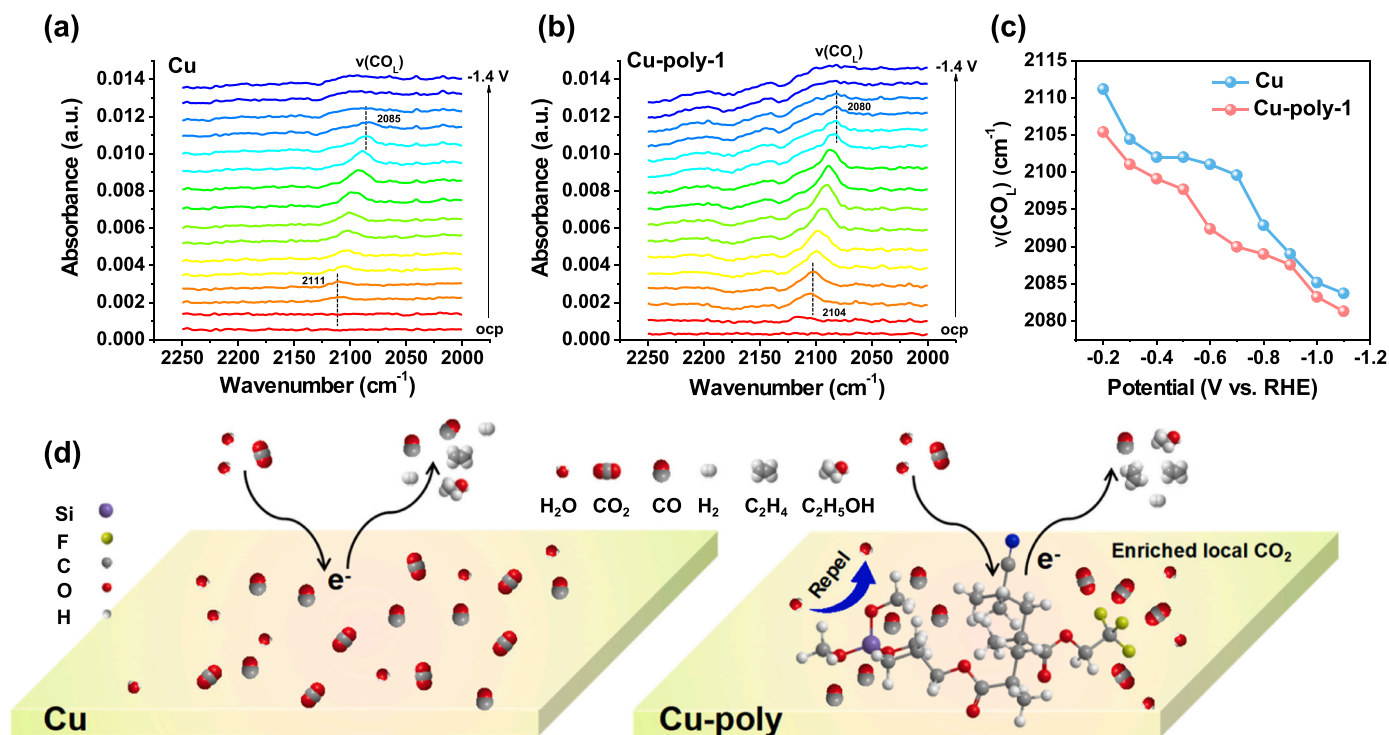
## 4. Conclusion

In summary, we demonstrated a free radical thermal polymerization method for the facile synthesis of polymers coating Cu catalysts. The modified Cu NPs present enhanced selectivity and current density of C<sub>2+</sub> products in CO<sub>2</sub>RR as compared to bare Cu NPs. Combining in situ infrared spectroscopic analysis and DFT calculations, the improved catalytic performances could be attributed to the enhanced coverage of \*CO and decreased formation energy of \*COCOH intermediates. Consequently, Cu-poly-1 delivers an excellent CO<sub>2</sub>RR performance of C<sub>2+</sub> products with a Faradaic efficiency of 71.08 % at a cell voltage of –3.98 V using MEA electrolyzer. This work offers a novel strategy for fabricating polymers modified Cu-based catalyst for CO<sub>2</sub> electrochemical reduction and provides a promising pathway to tuning the selectivity of C<sub>2+</sub> products through the regulation of electrochemical microenvironment.





**Fig. 3.** (a) Schematic illustration of the MEA cell configuration, using Cu-poly-1/2 and NiFe LDH as cathode and anode catalyst separately in contact with the AEM. (b) The FE and cell voltage of (b) Cu-poly-1 and (c) Cu with respect to the applied total current density. (d) FE of H<sub>2</sub>, C<sub>1</sub>, and C<sub>2+</sub> products from the CO<sub>2</sub>RR on Cu (faint yellow), Cu-poly-1 (pale green), and Cu-poly-2 (light purple) at current density of 500 mA cm<sup>-2</sup>.



**Fig. 4.** In situ ATR-SEIRAS spectra of CO<sub>2</sub>RR on the (a) Cu NPs and (b) Cu-poly-1 electrodes in CO<sub>2</sub>-saturated 1 M KHCO<sub>3</sub>. (c) Stark effects of the linearly adsorbed \*CO (CO<sub>L</sub>) on Cu NPs and Cu-poly-1 electrodes. (d) Schematic illustrations of the CO<sub>2</sub>RR mechanism on the Cu NPs and Cu-poly electrodes.

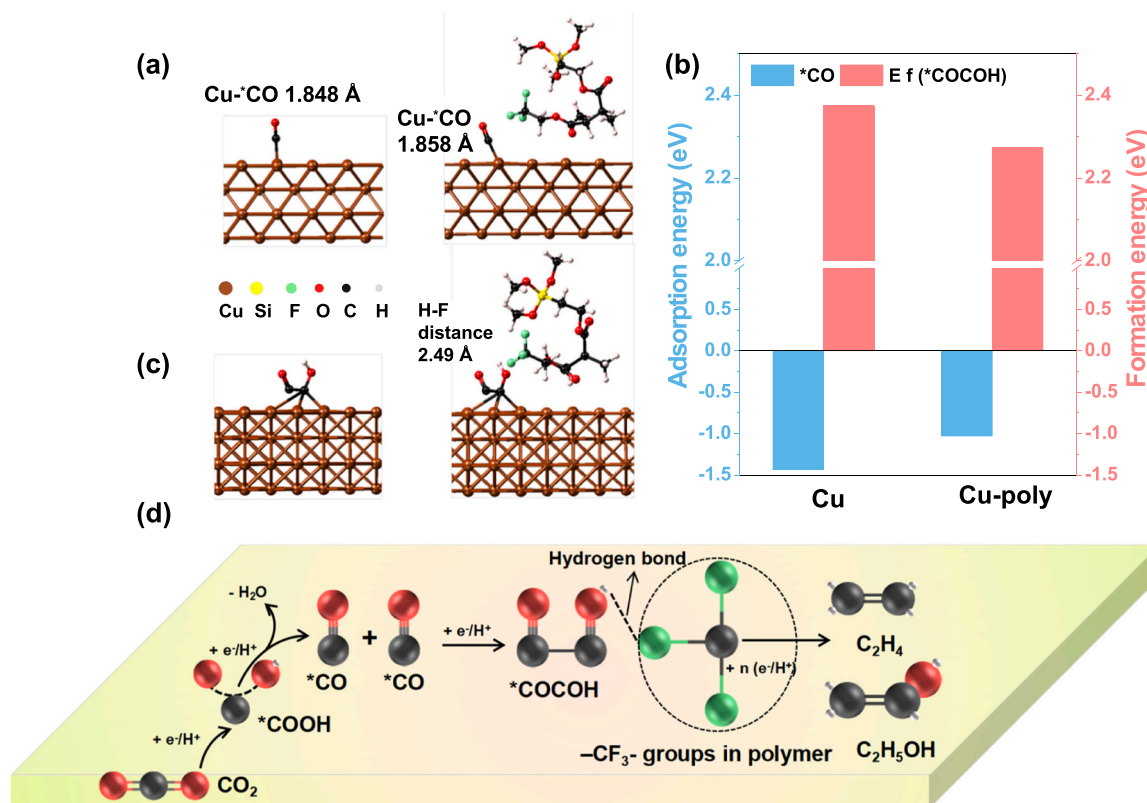


Fig. 5. Optimized adsorption configuration of (a)  $^*\text{CO}$  and (c)  $^*\text{COCO}$  on Cu and Cu-poly. (b) The adsorption energy of  $^*\text{CO}$  and formation energy of  $^*\text{COCO}$  on Cu and Cu-poly. (d) Proposed reaction pathway for  $\text{CO}_2\text{RR}$  to  $\text{C}_2+$  products on Cu-poly.

#### CRediT authorship contribution statement

**Tete Zhao:** conceptualization, experiments, visualization, writing-original draft. **Xupeng Zong:** DFT calculations and formal analysis. **Jiuding Liu and Jiale Chen:** software and visualization. **Keqiang Xu:** formal analysis. **Xiao Wang, Jiexi Chen and Wutong Yang:** experiments and formal analysis. **Meng Yu:** writing-review & editing, formal analysis. **Fangyi Cheng:** conceptualization, writing-review & editing, supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123281](https://doi.org/10.1016/j.apcatb.2023.123281).

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